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(54) Title: ANTIFOULING COATING COMPOSITIONS

(57) Abstract

An antifouling coating composition containing a biocide for marine organisms comprises as binder a polymer having pendent triorganosilyl carboxylate groups. To inhibit gelation of the composition during storage the coating composition also contains a monoamine having at least four carbon atoms or a quaternary monoammonium compound.

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# ANTIFOULING COATING COMPOSITIONS

## Technical Field

This invention is concerned with antifouling coating compositions used on surfaces likely to come into contact with marine fouling organisms such as algae, seaweed and barnacles, for example on ships or boats or on the outfalls for cooling water from power stations. Such coating compositions generally comprise a biocide for marine organisms and a binder polymer. More particularly, it relates to compositions capable of forming a coating film having an improved binder polymer.

## Background Art

The most successful antifouling paints in recent years have been self-polishing antifouling paints using binders which are linear polymers containing pendent side groups (hereinafter called "leaving groups") which are liberated from the polymer by reaction with seawater, the residual polymer being sufficiently dispersible or soluble in seawater to be swept away from the paint surface, exposing a fresh layer of the binder able to undergo a similar reaction with seawater. Such paints are described for example in British Patent 1457590. The gradual thinning of the paint film controls the release of a biocide active against fouling. The well-known benefits of such self-polishing paints are that the paint film tends to at least retain its initial smoothness and that the biocide contained in the paint tends to be delivered from the surface at a more uniform or constant rate.

The only commercially significant self-polishing paints employ binders which comprise triorganotin ester leaving groups. The triorganotin provides some of the biocidal action of the paints and the triorganotin ester readily undergoes the hydrolysis on which the self-polishing action is dependant. The biocidal activity can be augmented by other antifouling substances dispersed or

dissolved in the paint film. There may be advantages in replacing some or all of the triorganotin ester leaving groups by other leaving groups, which are not necessarily biocidal, both for cost reasons and because the powerful biocidal effects of triorganotin may not be desired.

International Patent Application WO84/02915, for example, discloses an antifouling paint having a hydrolysable film-forming water-insoluble seawater-erodible polymeric binder having recurring groups represented by the formula:

$$\left( -CH_2-\underset{\displaystyle COOR}{\overset{\displaystyle X}{\underset{|}{\overset{|}{C}}}}- \right) \left( B \right)$$

where X is hydrogen or methyl, R is a substituted alkyl, aryl, aralkyl or triorganosilyl moiety and B is the residue of an ethylenically unsaturated comonomer. WO84/02915 describes a wide range of groups R, but it has been found in practice that the less readily hydrolysable groups R such as benzyl, aminoalkyl and haloalkyl groups do not give a polymer which dissolves in seawater. WO84/02915 also describes hydrolysable groups R which are triorganosilyl groups and these are further described in US Patent 4593055. The triorganosilyl groups undergo rapid hydrolysis, but this can give rise to gelation of the paint composition on storage and undesirably rapid dissolution of the paint from a ship's hull in use.

Japanese published unexamined patent application 1-146969 describes an antifouling coating containing a copolymer of 10-90 molar % triorganosilyl acrylate or methacrylate units and 0.1-10 molar % tertiary aminoalkyl acrylate or methacrylate units.

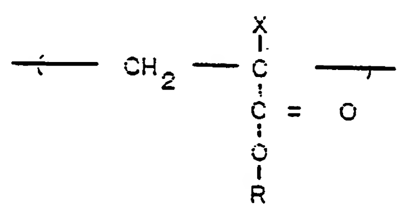
<u>Disclosure of Invention</u>

An antifouling coating composition according to the present invention containing a biocide for marine organisms

and comprising as binder a polymer having pendent triorganosilyl carboxylate groups, is characterised in that the coating composition contains a monoamine having at least 4 carbon atoms or a quaternary monoammonium compound.

The amine or quaternary ammonium compound inhibits gelation of the coating composition during storage. Paints containing a polymer having pendent triorganosilyl carboxylate groups may be liable to gelation during storage, particularly when the paint contains a metal compound as pigment, for example a copper or zinc compound such as cuprous oxide. The amine or quaternary ammonium compound also controls the rate of dissolution of the coating in use on a ship moving through seawater, prolonging the length of time for which the coating is effective.

The binder polymer is preferably a triorganosilyl acrylate or methacrylate polymer containing repeat units of the formula:



where X represents H or $CH_3$ and R represents a triorganosilyl moiety of the formula $Si(R')_3$, where the groups R', which can be the same or different, represent straight-chain or branched alkyl groups having 1 to 10 carbon atoms or phenyl groups.

The polymer is preferably produced by addition polymerisation of a triorganosilyl acrylate or methacrylate of the formula:

$$CH_2 = \overset{\overset{\displaystyle X}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R \qquad (I)$$

where R has the above meaning, using a free radical catalyst such as an azo compound or a peroxide, preferably in solution in an organic solvent. Examples of monomers of the formula (I) are tributylsilyl acrylate, triphenylsilyl acrylate, phenyldimethylsilyl acrylate, diphenylmethylsilyl acrylate, tri-isopropylsilyl acrylate and trimethylsilyl acrylate, and the corresponding methacrylates. Examples of suitable solvents are an aromatic hydrocarbon such as xylene or toluene, optionally mixed with an aliphatic hydrocarbon such as white spirit, an ester such as butyl acetate, ethoxyethyl acetate or methoxypropyl acetate, an alcohol such as butanol or butoxy-ethanol, or a ketone such as methyl isobutyl ketone or methyl isoamyl ketone.

The triorganosilyl acrylate or methacrylate monomer is generally copolymerised with one or more ethylenically unsaturated comonomers which do not undergo hydrolysis in seawater, for example acrylic esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate or 2-ethyl hexyl methacrylate, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl chloride or vinyl pyridine. Units of the triorganosilyl acrylate or methacrylate monomer can for example form 15 to 60 mole % of the resulting copolymer, preferably 20 to 45 mole %.

The polymer binder can alternatively be formed by reacting a carboxylic-acid-functional polymer, for example a copolymer of acrylic or methacrylic acid with an ethylenically unsaturated comonomer of the type described above, with a triorganosilyl compound such as a hexa-alkyl disilazane or a bis(triorganosilyl) urea.

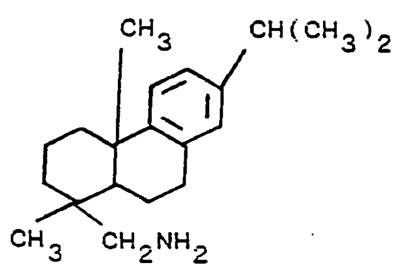
The polymer binder can alternatively be a block copolymer of a triorganosilyl acrylate or methacrylate polymer with polyether or polymethane blocks or blocks of another addition polymer such as polymethyl methacrylate as described in US Patent 4957989.

The monoamine used in the coating composition is preferably a primary amine, although a secondary or tertiary amine can be used. The amine or quaternary ammonium compound preferably includes at least one organic group having at least 8 carbon atoms, more preferably 8 to 20 carbon atoms. Such amines and quaternary ammonium compounds generally have the additional advantage that they are toxic to marine organisms. Primary amines having at least 8 carbon atoms are particularly preferred.

The monoamine can for example be a diterpene-derived amine of the formula:

$$R^1 - \underset{}{\overset{R^2}{\overset{|}{N}}} - R^3$$

where $R^1$ is a monovalent hydrocarbon group derived from a diterpene and $R^2$ and $R^3$ are each independently hydrogen, an alkyl group having 1 to 18 carbon atoms or an aryl group having 6 to 12 carbon atoms. These amines are usually toxic. Such an amine is preferably derived from rosin. A primary amine derived from rosin is dehydroabietylamine sold commercially as "Rosin Amine D". Its main constituent is



A corresponding secondary or tertiary amine, for example an N-methyl or N,N-dimethyl derivative of Rosin Amine D, can alternatively be used.

The monoamine can alternatively be an aliphatic amine containing an organic group of 12 to 20 carbon atoms, for example a straight-chain alkyl or alkenyl amine such as

dodecyl amine, hexadecyl amine, octadecyl amine or oleyl amine or mixtures of amines derived from aliphatic groups present in natural fats and oils such as tallow amine or hydrogenated tallow amine or coconut amine. These amines also are usually toxic.

Alternative monoamines which can be used are aralkyl-amines such as those sold commercially as "phenalkamines". The quaternary monoammonium compound can for example be a halide salt, e.g. hexadecyl trimethyl ammonium chloride.

The proportion of triorganosilyl polymer binder to amine or quaternary ammonium compound in the coating composition is preferably 98:2 to 40:60 by volume, most preferably 90:10 to 50:50. Amines having no film-forming properties are preferably used at no more than 25% based on the combined volume of polymer and amine, whereas film-forming amines such as the diterpene derivatives can be used at a higher proportion if desired.

If an amine or quaternary ammonium compound which is biocidal to marine organisms is used the resulting coating composition can be a clear antifouling varnish or can be pigmented. If a non-biocidal amine or quaternary ammonium compound is used the coating composition should contain a marine biocide. The coating preferably contains a pigment, and the same material may function simultaneously both as a marine biocide and as a pigment if a biocidal pigment is used. The coating composition preferably contains an organic solvent for the triorganosilyl polymer binder; if the polymer is prepared in solution the polymer solution produced can be used in preparing the paint.

The amine or quaternary ammonium compound can be premixed with the triorganosilyl polymer binder before addition of other components of the coating composition, or the binder polymer can simultaneously be mixed with the amine or quaternary ammonium compound and a pigment. For

example, the triorganosilyl polymer binder and the amine or quaternary ammonium compound can be mixed with pigment using conventional paint-blending procedures to provide a composition having a pigment volume concentration of, for example, 25 to 55%. The pigment is preferably a sparingly soluble pigment having a solubility in seawater of from 0.5 to 10 parts per million by weight and is preferably a metalliferous pigment. The pigment is most preferably a copper or zinc compound, for example cuprous oxide, cuprous thiocyanate, zinc oxide, zinc ethylene bis(dithiocarbamate), zinc dimethyl dithiocarbamate, zinc diethyl dithiocarbamate or cuprous ethylene bis(dithiocarbamate). These sparingly soluble pigments which are copper and zinc compounds are generally also marine biocides. The sparingly soluble metalliferous pigments produce water-soluble metal compounds on reaction with seawater so that the pigment particles do not survive at the paint surface. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate), which are highly effective biocidal pigments, can be mixed with zinc oxide, which is less effective as a biocide but dissolves slightly more rapidly in seawater.

The paint composition can additionally or alternatively contain a pigment which is not reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 part per million by weight) such as titanium dioxide or ferric oxide or an organic pigment such as a phthalocyanine pigment. Such highly insoluble pigments are preferably used at less than 40% by weight of the total pigment component of the paint, most preferably less than 20%.

The antifouling paint can also contain a non-metalliferous biocide for marine organisms, for example tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, a substituted isothiazolone or 2-methylthio-4-t-

butylamino-6-cyclopropylamino-s-triazine.

The antifouling coating composition of the invention is generally applied from a solution in an organic solvent; for example when the triorganosilyl polymer is prepared in an organic solvent the polymer solution can be used directly in the paint. It can optionally be diluted by further solvent, preferably selected from the solvents listed above.

The invention is illustrated by the following Example.

## Example

15 molar % phenyldimethylsilyl acrylate, 15 molar % trimethylsilyl methacrylate and 70 molar % butyl methacrylate were copolymerised as a 40% by weight solution in xylene at 70°C using azobisisobutyronitrile as initiator. The resulting triorganosilyl copolymer solution was mixed with pigments, structuring agents, Rosin Amine D and additional solvent in a high-speed disperser and ground to a particle size of 25 microns to produce an antifouling paint having the following formulation:

| | Per Cent by Weight |
|---|---|
| Triorganosilyl copolymer | 15.7 |
| Xylene | 31.0 |
| Methyl isoamyl ketone | 14.9 |
| Cuprous oxide | 28.7 |
| Titanium dioxide | 3.4 |
| Structuring Agents (bentonite clay, zeolite and silica) | 1.7 |
| Rosin Amine D | 4.6 |

A sample of the paint produced was stored in a can at 45°C for 22 days. A slight skin formed at the surface of the paint but the paint was still sprayable. By comparison, a paint (A) based on the same copolymer and having

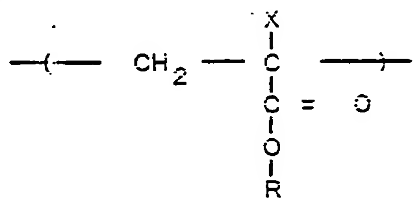
the same pigment volume concentration but containing no Rosin Amine D had gelled on storage and was not sprayable.

Further samples of the paints produced were applied as two stripes 90 microns thick on a disc. The disc was rotated in seawater for 30 days as a test designed to measure the rate of dissolution of the paints when used as a self-polishing antifouling paint. The thickness of the paint stripes was measured before and after the trial and the rate of polishing away of paint was calculated. The rate of dissolution of the paint of the invention was only 44% of that of the comparison paint (A).

CLAIMS

1. An antifouling coating composition containing a biocide for marine organisms and comprising as binder a polymer having pendent triorganosilyl carboxylate groups, characterised in that the coating composition contains a monoamine having at least four carbon atoms or a quaternary monoammonium compound.

2. An antifouling coating composition according to claim 1, characterised in that the binder polymer is a triorganosilyl acrylate or methacrylate polymer containing repeat units of the formula:



where X represents H or $CH_3$ and R represents a triorganosilyl moiety of the formula $Si(R')_3$, where the groups R', which can be the same or different, represent straight-chain or branched alkyl groups having 1 to 10 carbon atoms or phenyl groups.

3. An antifouling coating composition according to claim 2, characterised in that the binder polymer is a copolymer of a triorganosilyl acrylate or methacrylate monomer with one or more ethylenically unsaturated comonomers which do not undergo hydrolysis in seawater.

4. An antifouling coating composition according to claim 3, characterised in that units of the triorganosilyl acrylate or methacrylate monomer form 15 to 60 mole% of the copolymer.

5. An antifouling coating composition according to claim 3, characterised in that units of the triorganosilyl

acrylate or methacrylate monomer form 20 to 45 mole% of the copolymer.

6. An antifouling coating composition according to any of claims 1 to 5, characterised in that the amine or quaternary ammonium compound includes at least one organic group having at least 8 carbon atoms.

7. An antifouling coating composition according to claim 6, characterised in that an amine is used which has the formula:

$$R^1 - \overset{\displaystyle R^2 \atop |}{N} - R^3$$

where $R^1$ represents a monovalent hydrocarbon group derived from a diterpene and $R^2$ and $R_3$ each independently represent hydrogen, an alkyl group having 1 to 18 carbon atoms or an aryl group having 6 to 12 carbon atoms.

8. An antifouling coating composition according to claim 6, characterised in that an amine is used which is an aliphatic amine containing an organic group of 12 to 20 carbon atoms.

9. An antifouling coating composition according to any of claims 1 to 8, characterised in that the proportion of triorganosilyl polymer binder to amine or quaternary ammonium compound is 98:2 to 40:60 by volume.

10. An antifouling coating composition according to claim 9, characterised in that the proportion of triorganosilyl polymer binder to amine or quaternary ammonium compound is 90:10 to 50:50 by volume.

11. An antifouling coating composition according to any of claims 1 to 10, characterised in that it contains as pigment a copper or zinc compound having a solubility in sea water of from 0.5 to 10 parts per million by weight.

12. An antifouling coating composition according to claim 11, characterised in that the pigment is cuprous oxide.

13. A process for preparing an antifouling coating composition containing a biocide for marine organisms and comprising as binder a polymer having pendent triorganosilyl carboxylate groups, characterised in that a monoamine having at least four carbon atoms or a quaternary monoammonium compound is incorporated into the composition.

14. A process according to claim 13, characterised in that the amine or quaternary ammonium compound is premixed with the binder before addition of other components of the coating composition or is mixed simultaneously with the binder and a pigment.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/00428

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

$IPC^5$: C 09 D 5/14

**II. FIELDS SEARCHED**

Minimum Documentation Searched [7]

| Classification System | Classification Symbols |
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT** [9]

| Category [*] | Citation of Document, [11] with indication, where appropriate, of the relevant passages [12] | Relevant to Claim No. [13] |
|---|---|---|
| A | Patent Abstracts of Japan, volume 13, nr. 402 (C-633)(3750), 6 September 1989 & JP, A, 1146969 (TOSHIBA SILICONE CO), 8 June 1989 cited in the application --- | |
| A | WO, A, 8402915 (M & T CHEMICALS INC.) 2 August 1984 cited in the application --- | |
| A | EP, A, 0279505 (NIPPON OIL & FATS CO.) 4 January 1989 ------------- | |

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**IV. CERTIFICATION**

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| EUROPEAN PATENT OFFICE | MISS T. TAZELAAR |

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| | | AU-A- 2497184 | 15-08-84 |
| | | EP-A,B 0131626 | 23-01-85 |
| | | JP-T- 60500452 | 04-04-85 |
| | | US-A- 4594365 | 10-06-86 |
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| | | US-A- 4593055 | 03-06-86 |
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